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METHOD FOR PRODUCTION OF BISTHIOESTERS

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PATENT NO. 2 771 411 A1

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List of documents cited in the Preliminary Search Report:	Refer to the end of the present section

METHOD FOR PRODUCTION OF BISTHIOESTERS

[Procédé de fabrication de bisthioesters]

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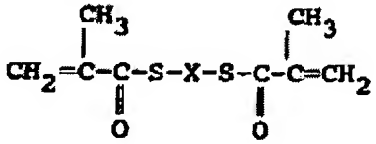
Applicant:	Elf Atochem Inc., France

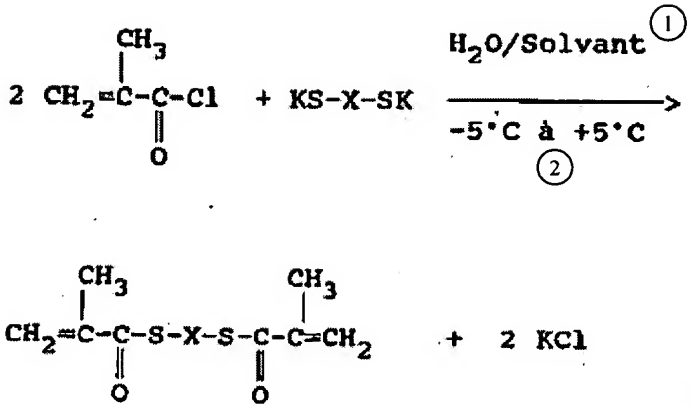
The present invention refers to a method for production of bisthioesters represented by formula (I):



(I)

in which X represents $-CH_2CH_2-S-CH_2CH_2-$; $-CH_2CH_2-$ or $-CH_2CH_2CH_2-$.

Usually, compounds with formula (I) in which X represents $-CH_2CH_2-$ or — $CH_2CH_2-S-CH_2CH_2-$ described in EP-B-273 661are prepared by reacting together ethane dithiol or dimercaptoethyl sulfide, respectively, or the corresponding potassium salt and methacryloyl chloride according to the reaction:



Key: 1 Solvent
2 To

This route of synthesis has several drawbacks:

(1) methacryloyl chloride is unavailable on an industrial scale;

(2) the method is polluting because it creates aqueous effluents of KCl;

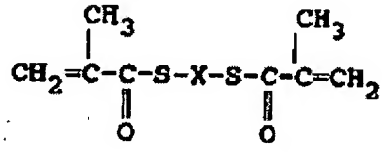
(3) the chemical instability of methacryloyl chloride requires its redistillation before use to remove an impurity formed by a cyclic compound resulting from the reaction between two molecules of methacryloyl chloride during storage.

American Patent US-A-5 384 379 describes a route of synthesis of compounds (I) from methacrylic anhydride and a corresponding potassium salt of dimercaptan in a solvent medium (such as methyl t-butyl ether). This method has been reproduced in the laboratory: decantation problems were encountered, matched with an average yield essentially due to insufficient conversion of starting products.

FR-A-2 269 523 describes the synthesis of thioesters with alpha, beta unsaturation by reaction of a chloride, fluoride, bromide or carboxylic acid anhydride with alpha, beta unsaturation with a mercaptan, in the presence of a catalyst chosen especially from transition metal halides (Ti, V, Cr, Mn, Zr, ...) and boron and antimony fluorides (SbF_3, BF_3). These catalysts pose problems with post-reaction treatment of heavy metal residues.

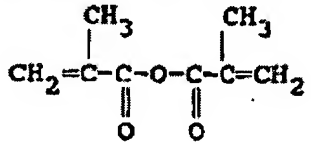
The applicant company has developed a new method for production of compounds of formula (I) that makes it possible to be free of all the drawbacks described above.

In fact, the goal of the present invention is a production method of bisthioester of formula (I):



(I)

in which X represents $-CH_2CH_2-S-CH_2CH_2-$; $-CH_2CH_2-$ or $-CH_2CH_2CH_2-$, characterized by the fact that the methacrylic anhydride



is reacted with a dimercaptan of formula (II):

$$HS-X-SH \qquad (II)$$

in which X is as defined above.

In conformance with a preferred embodiment, the reaction is conducted in the presence of a cation exchange resin in H^+ form as catalyst.

Then, the ion exchange resin in H^+ form as catalyst is used especially at 2 to 15% by weight relative to the total weight of the methacrylic anhydride and dimercaptan of formula (II). Advantageous resins are those obtained by sulfonating a styrene and divinylbenzene copolymer.

The molar ratio of methacrylic anhydride/dimercaptan of formula (II) is located especially in the range of 1.8 to 2.2.

The method according to the present invention is advantageously conducted at a temperature of 35 to 80°C.

The methacrylic anhydride is advantageously used while being stabilized by a stabilizer such as bis-tert-butyl hydroxytoluene.

The following example illustrates the present invention without, however, limiting the scope.

Example

In a three-necked round-bottom flask is loaded:

- 6 g of the H^+ resin sold under the trademark "Amberlyst" 15;
- 70.1 g of methacrylic anhydride stabilized with 20,000 ppm of bis-tert-butyl hydroxytoluene.

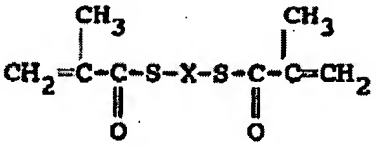
This is brought to 60°C under bubbling of nitrogen. Then over 30 min, 38.5 g of dimercaptoethyl sulfide are introduced. The course of the reaction is followed by gas chromatography. After 17 hours of reaction, all the methacrylic anhydride involved has disappeared. The reaction medium is cooled to room temperature and it is filtered.

After distillation of the filtrate under reduced pressure to remove the methacrylic acid, the desired bisthioester is obtained at 85% yield and 90% purity.

The methacrylic acid may also be removed by neutralization with sodium hydroxide.

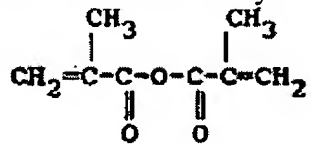
Claims

1. Method for production of bisthioester of formula (I):

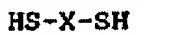


(I)

in which X represents $-CH_2CH_2-S-CH_2CH_2-$; $-CH_2CH_2-$ or $-CH_2CH_2CH_2-$, characterized by the fact that the methacrylic anhydride



is reacted with a dimercaptan of formula (II)



(II)

in which X is such as defined above.

2. Method according to Claim 1 characterized by the fact that the reaction is conducted in the presence of a cation ion exchange resin in H^+ form as catalyst.

3. Method according to Claim 2 characterized by the fact that the ion exchange resin in H+ form is used as catalyst at 2 to 15% by weight relative to the total weight of the methacrylic anhydride and the dimercaptan (II).

4. Method according to one of Claims 2 and 3, characterized by the fact that the ion exchange resin is chosen from those obtained by sulfonating a copolymer of styrene and divinylbenzene.

5. Method according to one of Claims 1 to 4 characterized by the fact that the methacrylic anhydride/dimercaptan (II) molar ratio is located in the range of 1.8 to 2.2.

6. Method according to one of Claims 1 to 5 characterized by the fact that it is conducted at a temperature of 35 to 80°C.

7. Method according to one of Claims 1 to 6 characterized by the fact that maleic anhydride is used in the stabilized state.

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SEARCH REPORT
established on the basis of the most recent
claims filed before the start of the search

2771411
Application Number
FA 549794
FR 9714937

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication where appropriate, of relevant passages	Claims concerned in the examined document	
A	US 4 810 812 A (T. MATSUDA, ET AL.) March 7, 1989 * Examples 1,5 * ---	1	
A	US 5 488 128 A (M. BADER, ET AL.) January 30, 1996 * Claim 1; example 1 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.[6]) C07C
Date of completion of the search July 31, 1998		Examiner R. English	

CATEGORY OF CITED DOCUMENTS

X: Particularly relevant if taken alone.

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O: Non-written disclosure.

P: Intermediate document.

T: Theory or principle underlying the invention.

E: Earlier patent document, but published on, or after the filing date.

D: Document cited in the application.

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